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In Situ Insight into Reversible O₂ Gas-Solid Reactions

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In Situ Insight into Reversible O₂ Gas-Solid Reactions

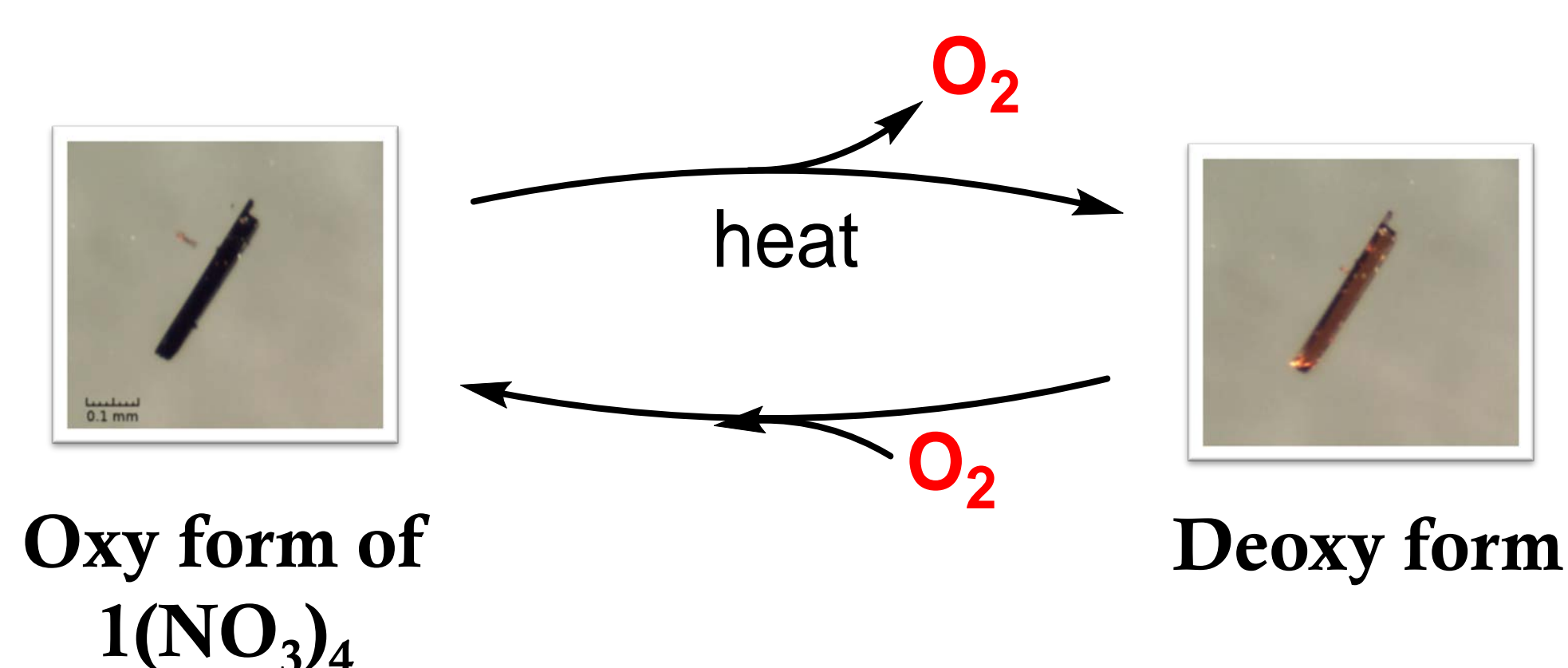
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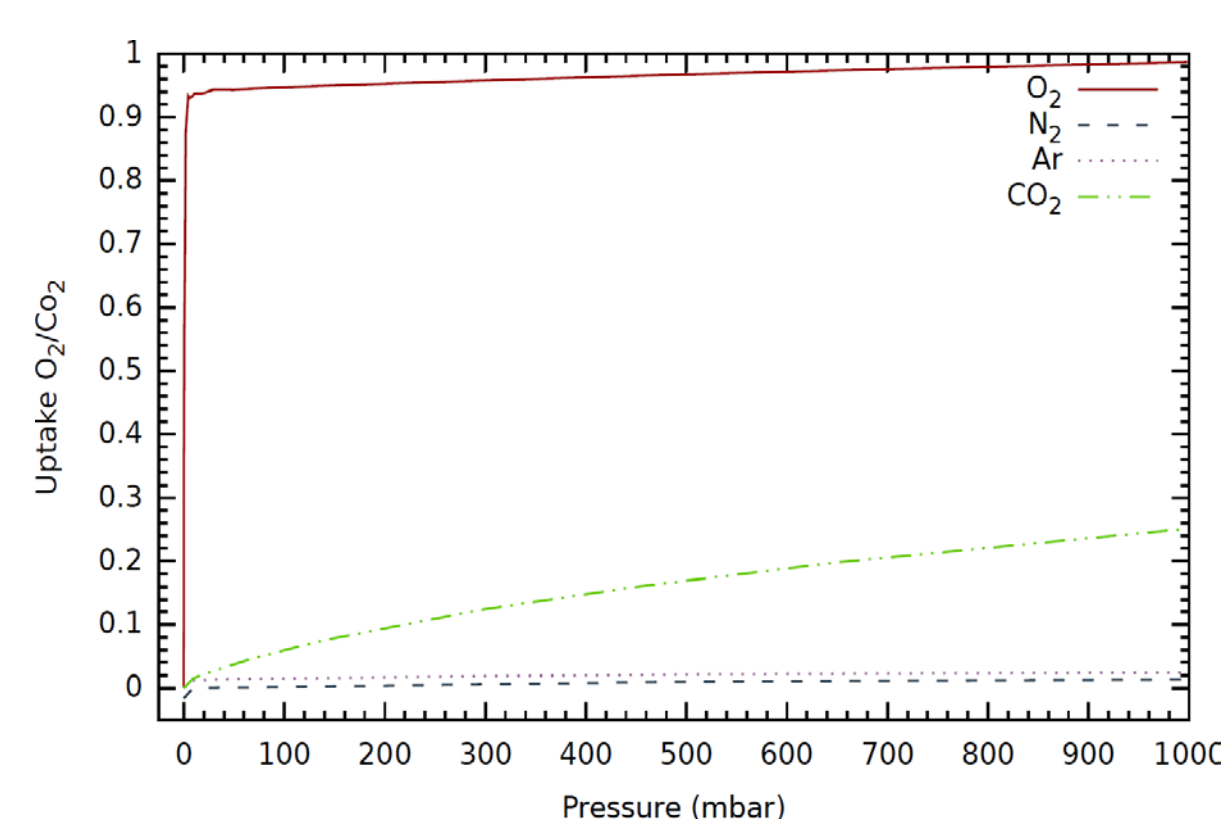
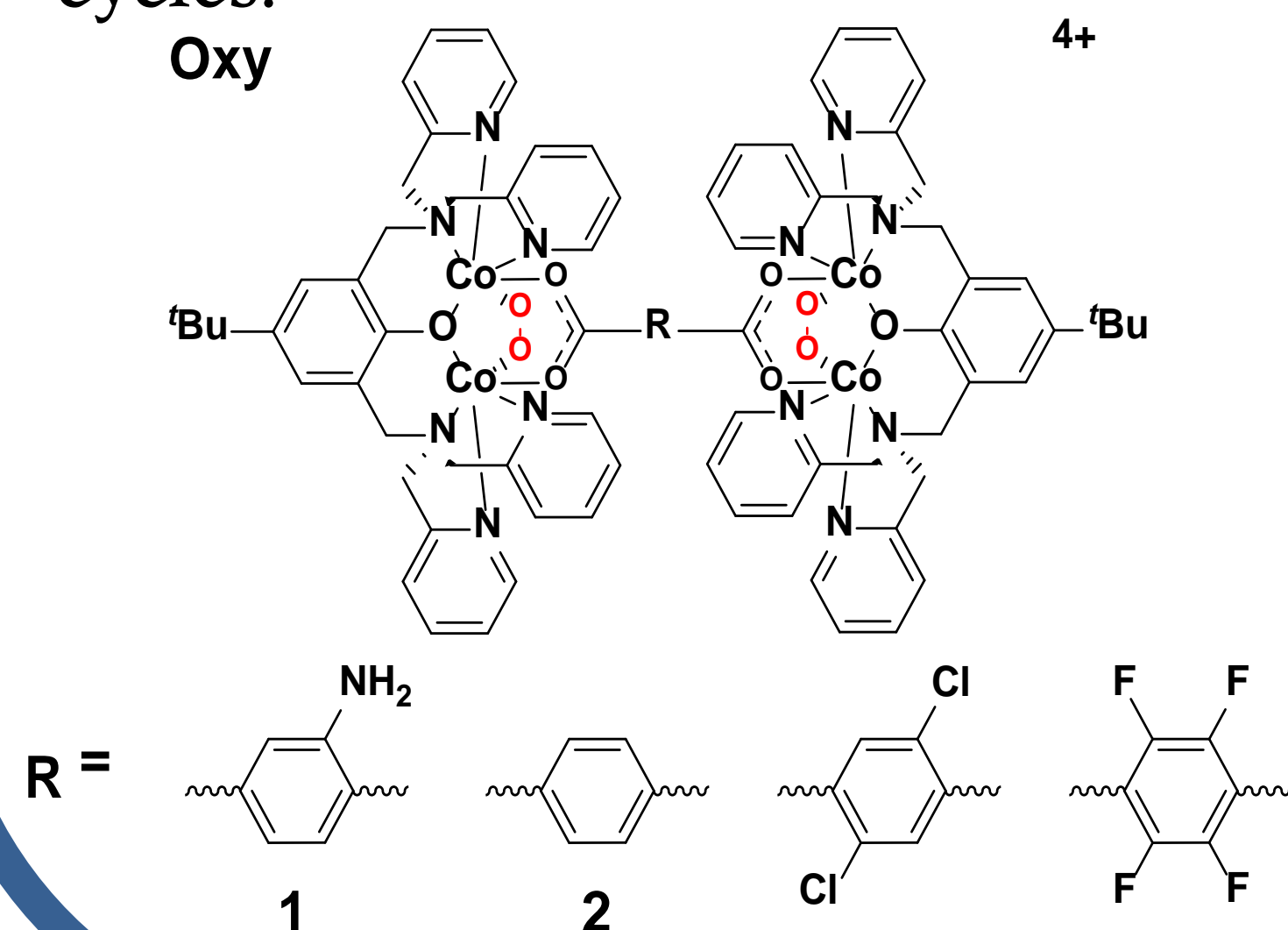
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Crystals that Breathe

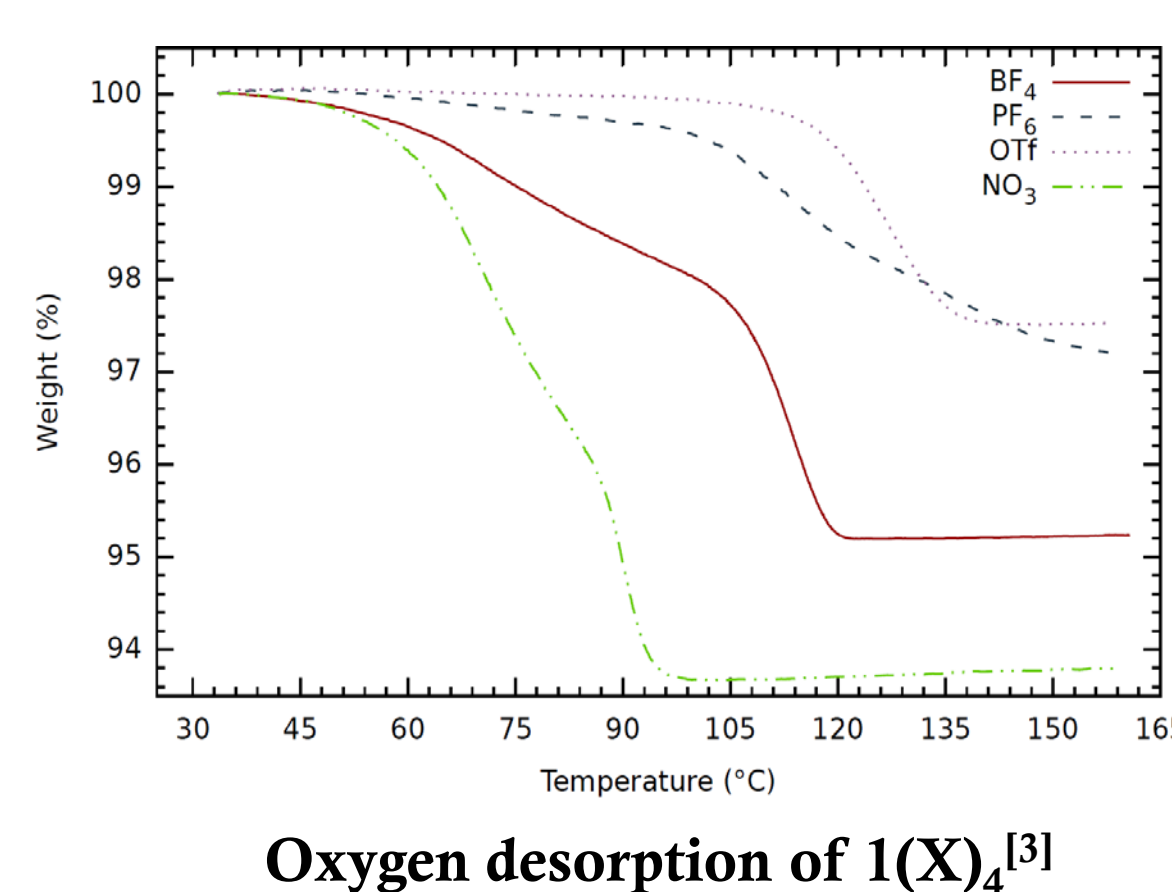


A series of crystalline solids containing cationic tetracobalt complexes spontaneously **chemisorb** O₂ from the air.^[1] The sorption/desorption of O₂ is **reversible** and **selective** and occurs without the material losing its (single) crystallinity over several cycles.^[2-4]



Selective gas sorption for 2(PF₆)₄^[2]

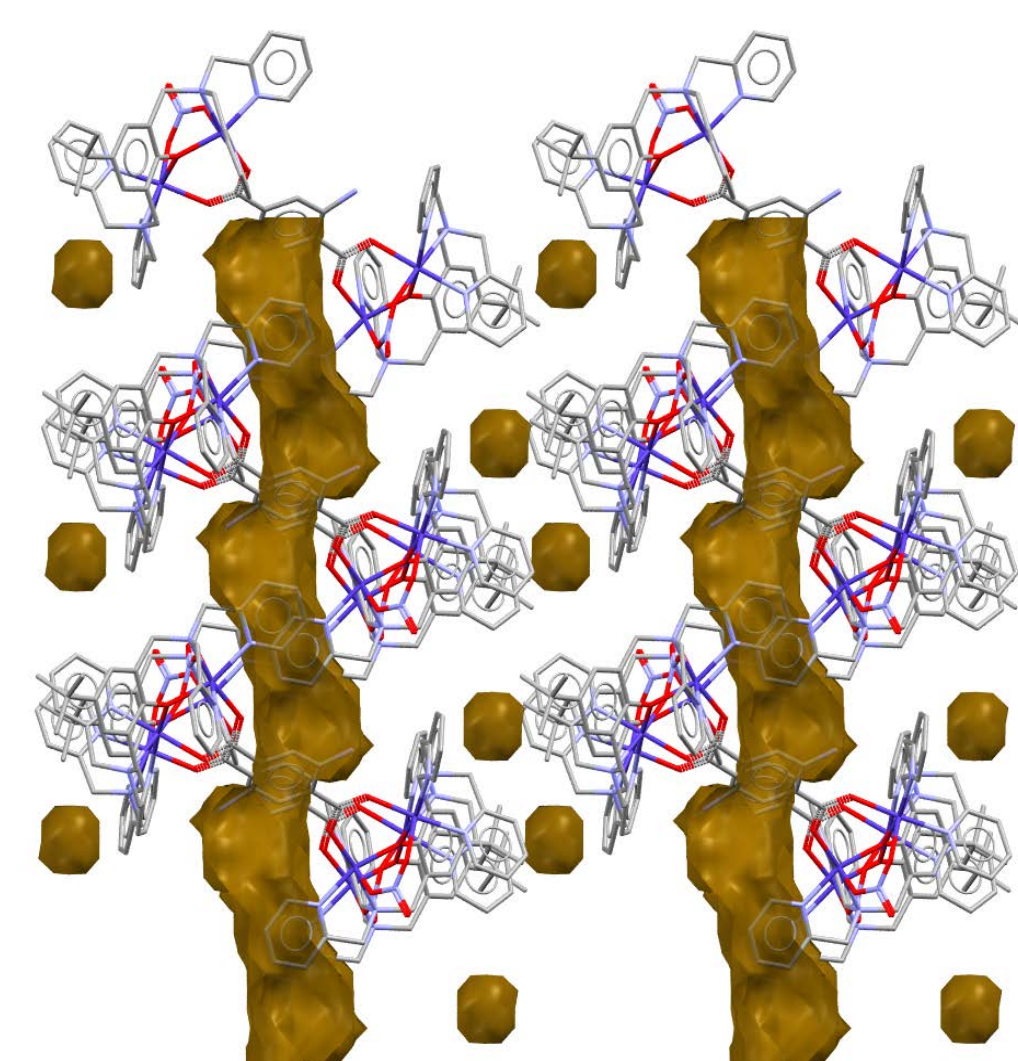
Phase Tweaking Overrides Molecular Tweaking



In the solid state the O₂ binding affinity is influenced strongly by the phase and counter anion, this is in contrast to solution state where the introduction of electron withdrawing groups on the co-ligands strongly affects O₂ affinity^{[2],[6]}.

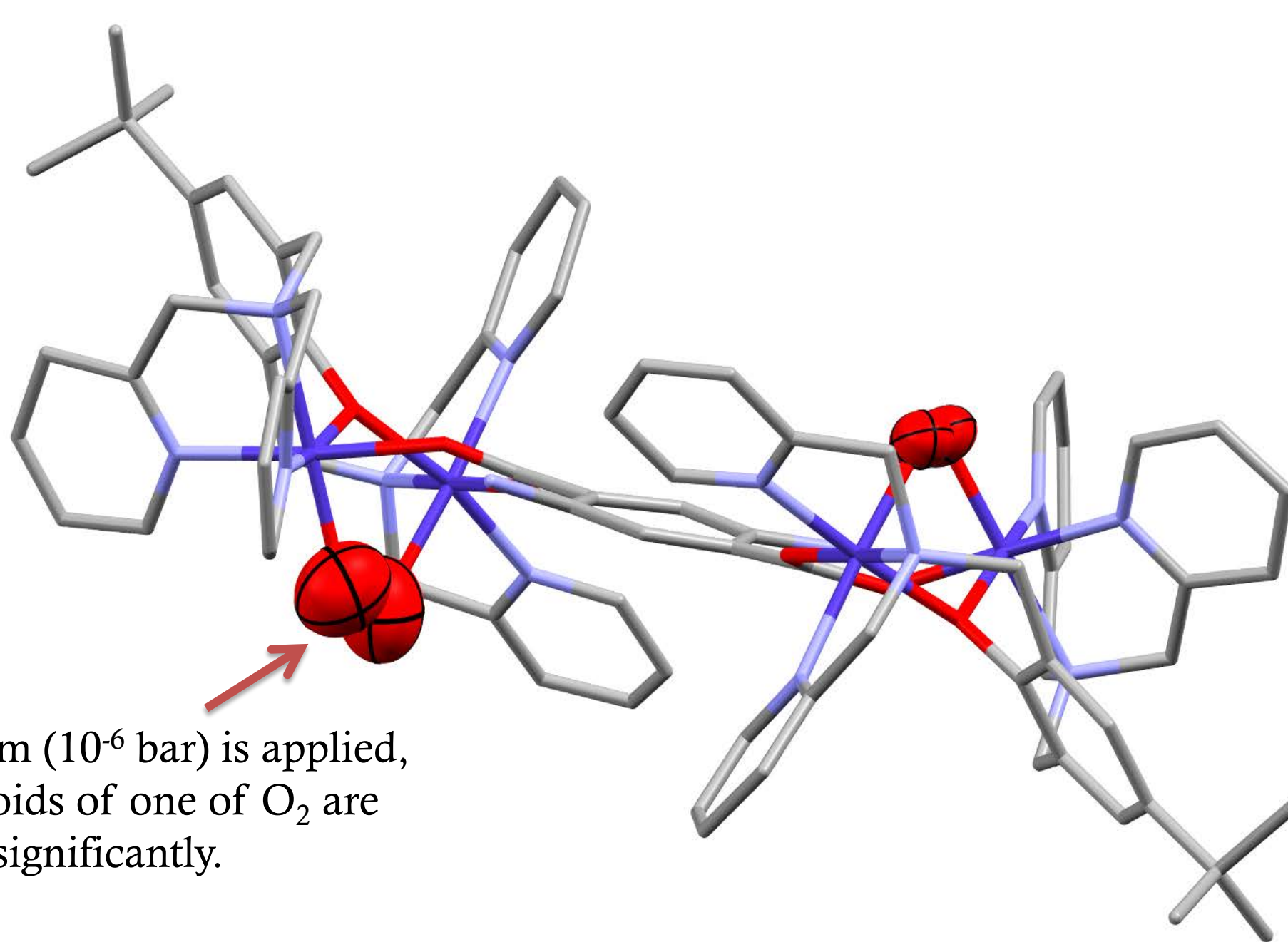
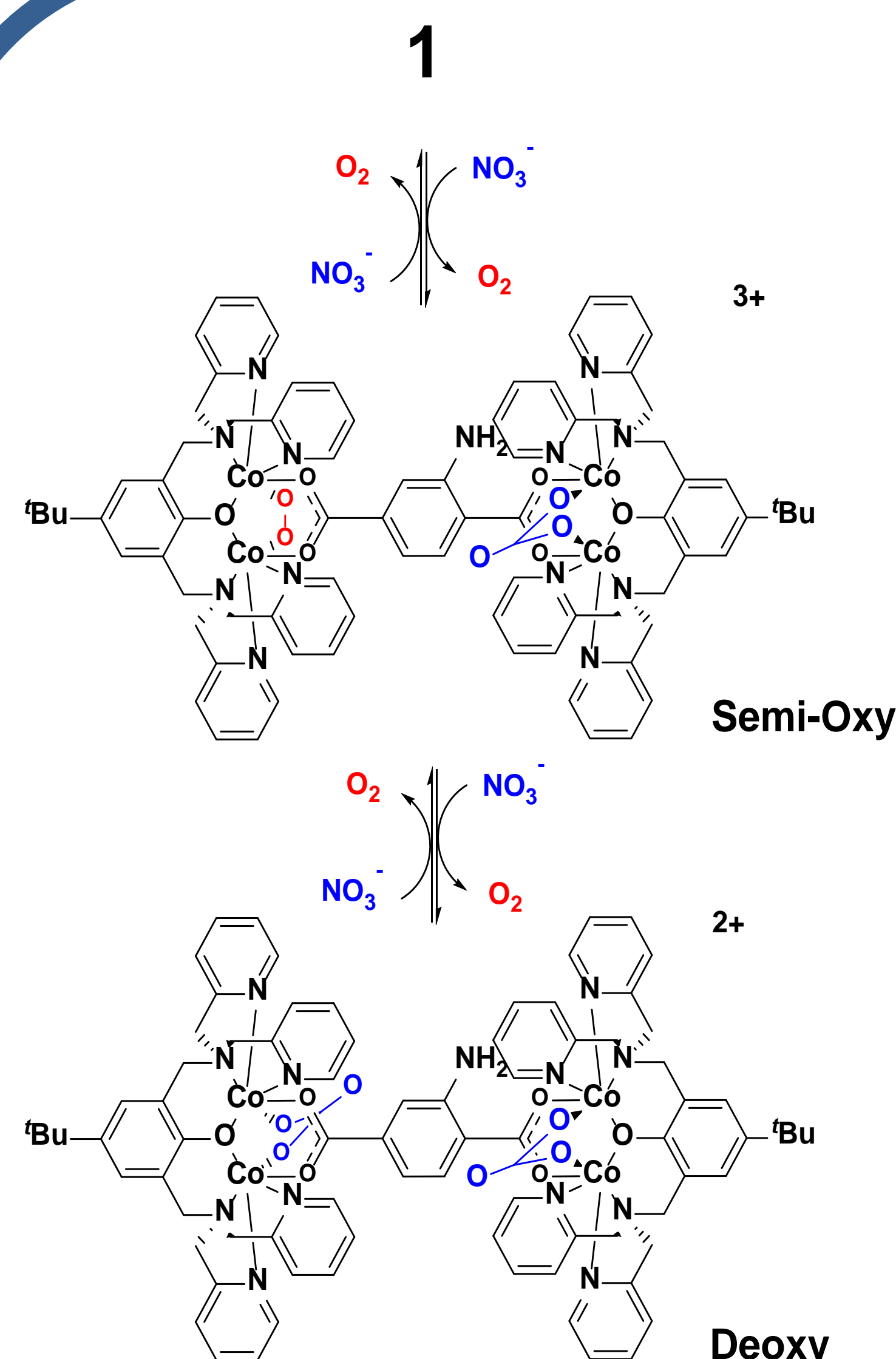
An obstacle race for O₂:

The gas cell experiment indicates the presence of a transient conduit through the crystals of the non-porous nitrate salt.



Packing of deoxy form of 1(NO₃)₄
Counter anions are removed to show conduits

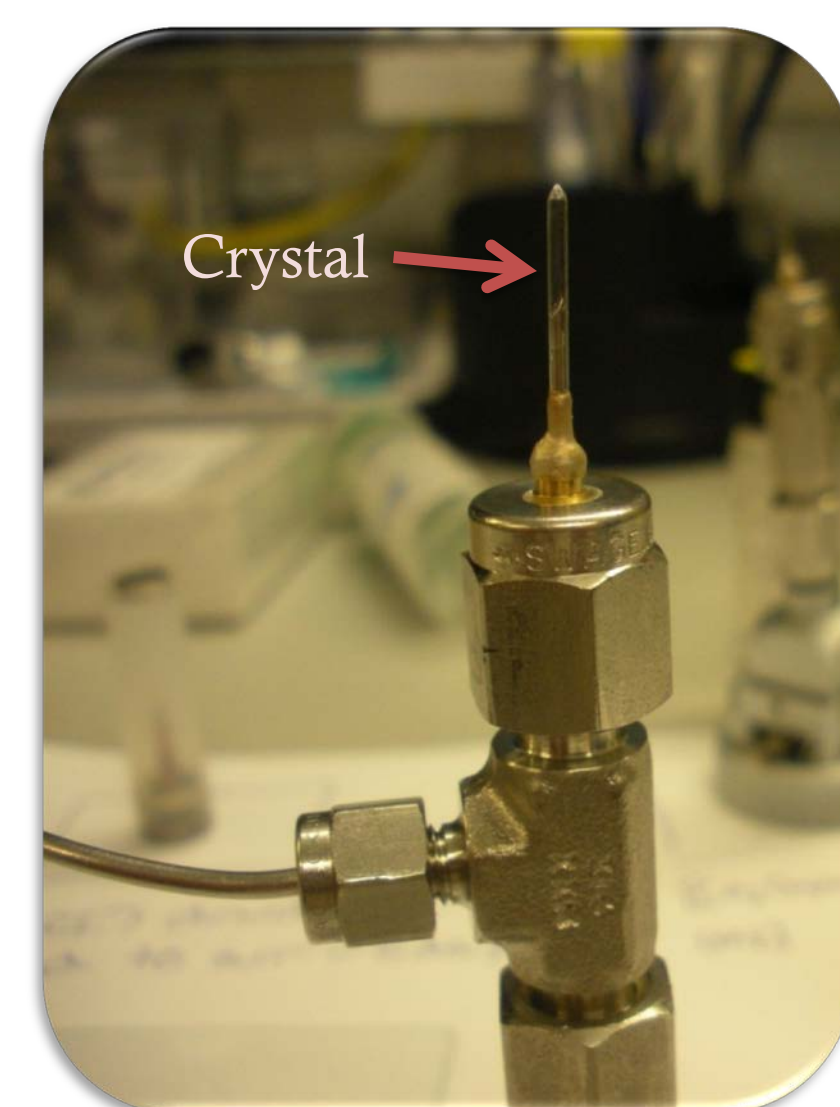
A Stepwise Gas-Solid Reaction



As vacuum (10⁻⁶ bar) is applied, the ellipsoids of one of O₂ are enlarged significantly.

The gas-cell setup at the synchrotron DIAMOND (beamline I19) enables crystallographic evidence that the reaction proceeds *via* a semi-oxy, thus we have detected two steps in the chemisorption process^[5].

The gas-solid single crystal to single crystal transformation^[4] shows that one nitrate per dioxygen moves 5-7 Å in the crystal lattice concomitant with O₂ sorption and release. The deoxy form contains nitrate anions bridging the dicobalt(II) sites^[3].



Work in Progress

- Insight into the O₂ sorption/desorption of other phases to investigate the role of non-coordinating counter anions
- Gas-solid reactions with other gasses (NO and H₂)
- Light triggered release of O₂?



^[1] M. Ghiladi, J. T. Gomez, A. Hazell, P. Kofod, J. Lumtscher, C. J. McKenzie, *Dalton Trans.* **2003**, 1320-1325. ^[2] P. D. Southon, D. J. Price, P. K. Nielsen, C. J. McKenzie, C. J. Kepert, *J. Am. Chem. Soc.*, **2011**, *133*, 10885-10891. ^[3] J. Sundberg, L. J. Cameron, P. D. Southon, C. J. Kepert, C. J. McKenzie, *Chem. Sci.* **2014**, *5*, 4017-4025. ^[4] <https://www.youtube.com/watch?v=gJbG9FvgX0U>. ^[5] C. Wegeberg, V. Jakobsen, M. Warren, A. D. Bond, C. J. McKenzie, *In preparation*. ^[6] M. S. Vad, F. B. Johansson, R. K. Seidler-Egdal, J. E. McGrady, S. M. Novikov, S. I. Bozhevolnyi, A. D. Bond, C. J. McKenzie, *Dalton Trans.* **2013**, *42*, 9921-9929. Picture of Aquaman: <http://milaboo.deviantart.com/art/Aquaman-344553900>